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Sustainable Alternatives to Petroleum-derived Substances for Preventing Fertiliser Caking

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Abstract

This study addresses the environmental concerns associated with the conventional anti-caking products by developing plant-based alternatives to petroleum-derived materials. Conventional anti-caking products often leave long-lasting residues in soil, which can transform into harmful, mutagenic forms, posing environmental risks. To mitigate these issues, eco-friendly compositions were developed and applied as coating to two different types of compound fertilisers, namely, 20.20.0 (7/13) and 15.15.15 (15/0), which are known for their high caking tendency. The coated fertilisers were subjected to several tests to evaluate their caking tendency, moisture absorption, dust formation, and crushing strength. The uncoated fertilisers exhibited a significant caking tendency, ranging from 30.89 %wt to 38.14 %wt, with dust formation between 1.91 %wt and 2.84 %wt, and crushing strength measuring between 473.8 and 593.0 g *per* granule. In contrast, the application of plant-based coatings improved product performance by significantly reducing the caking tendency to a range of 0–16.33 %wt, yielding results comparable to petroleum-derived coatings, which showed a tendency of 0–17.45 %wt. Notably, the most substantial improvement was observed when a coating containing stearylamine, plant-oils and waxes was applied, resulting in granules with a crushing strength of 4274.2–5318.0 g *per* granule and a reduction in dust formation. Additionally, the plant-based coatings exhibited low moisture absorption, remaining below 20 mg cm^{-2} indicating the presence of a moisture-repellent film.

Keywords

Abrasion, anti-caking agents, caking, fertilisers, sustainable coatings

1 Introduction

The two major challenges in agricultural production are meeting the food needs of the ever-increasing global population and mitigating climate change.[1] Fertilisers contribute significantly to the global food production. However, in recent years, the widespread and uncontrolled use of these fertilisers has led to inefficiencies and environmental problems.[2] Consequently, as fertiliser usage increases, it is essential to ensure their high quality to address issues such as caking, dust generation, and imbalanced nutrient distribution.[3] Improving the environmental compatibility of fertilisers can be achieved by developing fertiliser technologies that enhance nutrient release, physical properties, and other characteristics of fertilisers, thereby supporting sustainable agriculture.[4]

Currently, there is a growing interest in the use of plant-based and biodegradable coating materials for mineral fertilisers.[5] Research on biodegradable coatings is gaining importance with the upcoming European fertiliser standards, which are set to take effect in 2026.[6–7] Fertiliser coatings are essential for maintaining the physical quality of granules and are continuously being improved to accommodate new types of fertilisers, as well as future regulations concerning environmental and ecological health.[6] Biobased ingredients are considered more sustainable and environmentally friendly compared to petroleum-based materials. However, many commercially available coatings still consist of ingredients that may be unsustainable, costly, and ecologically harmful, such as paraffin or mineral oil.[3,6]

Caking is a detrimental phenomenon that is common in many industries, leading to economic losses, product degradation, process interruption, and reduced product quality.[8–9] Under conditions such as transport, handling, and storage, some solids tend to form lumps over extended periods, a process defined as "caking".[10] Fertiliser caking occurs due to the undesired agglomeration of granules through the formation of crystal or liquid bridges between them.[11] Measures to prevent caking can be achieved by controlling environmental conditions and using small amounts of non-toxic, effective anti-caking agents.[12] Anti-caking agents are used to provide free flowing properties by preventing the results of interparticle mechanisms triggered by ambient conditions such as humidity, temperature, storage time, and pressure.[13] Depending on their application, they are categorised into internal and external additives, such as coating agents, and they can take various physical forms, including inert powders, viscous liquids, liquids, or waxes.[14–15] Their primary function is to reduce contact between atmospheric moisture and the fertiliser surface through different mechanisms.[16–17] Coating agents are applied to the fertiliser surface, creating a hydrophobic layer that inhibits crystal growth, particle interaction, and moisture absorption, which initiates the caking process. Additionally, they help to reduce degradation and abrasion by forming a protective film on the granule surface.[18–19]

Commercial coating agents, typically based on petroleum-derived substances, may include oils, fatty acids,

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Table 1 – Control group fertilisers

Primary nutrients / %wt	NP-20.20.0 (7/13)	NPK-15.15.15 (15/0)	Source of nutrients	CAS No.
NH_4-N (Ammonium N)	7	15	Ammonium sulphate	7783-20-2
NH_2-N (Urea N)	13	0	Urea	57-13-6
P (as P_2O_5)	20	15	Phosphoric acid	7664-38-2
K (as K_2O)	0	15	Potassium chloride	7440-09-7

waxes, and surfactants such as primary fatty amines, and sometimes secondary and tertiary fatty amines, which are highly hydrophobic.[20–21] Aliphatic amines, in particular, reduce crystal-solution interface energy, making the fertiliser surface hydrophobic, which reduces moisture absorption and prevents agglomeration.[22–23] These materials, due to their cationic characteristics, facilitate the thorough dispersion of the coating on the fertiliser surface by interacting with anions like nitrate or sulphate salts, promoting strong adhesion.[24] They contain both polar and non-polar groups, they are amphiphilic compounds that prevent adhesion, reduce interfacial energy between the crystal fertiliser structure and moisture on the surface, and inhibit crystallisation.[25–26] In addition to surfactants, mineral and paraffin oils are commonly used in anti-caking agents but can leave persistent residues in the soil and pose environmental risks due to their highly aromatic components, such as polycyclic aromatic hydrocarbons (PAHs).[27–28] Therefore, there is a crucial need for more research on sustainable and eco-friendly substances for fertiliser coatings.[29–30] Beyond the environmental impact of petroleum-derived polymers, the depletion of petroleum resources necessitates replacing these materials with substances derived from renewable resources.[31] For example, plant oils are hydrophobic materials that can be optimised as film coatings. They are easily accessible, environmentally friendly, sustainable, and more degradable by soil microorganisms.[32–34]

To address the caking issue, the use of anti-caking agents is almost mandatory for the fertiliser industry. Fertilisers cannot be stored for extended periods without these additives. However, these agents are among the costliest and most fuel-dependent components produced outside the fertiliser industry. Since anti-caking agents play a crucial role in maintaining fertiliser quality and are often petroleum-based, causing environmental challenges, one step toward decarbonisation in the fertiliser industry could be the use of green additives. Petroleum-derived substances and low-degradability polymer coatings, which are widely used but harmful to the environment, will be prohibited under EU regulations starting in 2026. From a regulatory compatibility perspective, an important research study to provide alternative anti-caking agents is here presented. The aim of this study was to develop anti-caking coatings for nitrogenous fertilisers that comply with future regulations, such as those of the EU, and are environmentally friendly. The findings will provide significant input for the fertiliser industry, with the newly developed coatings serving as viable alternatives to conventional coatings. As EU regulations will require the use of biodegradable materials in fertilisers as of 2026, this research offers valuable insights for the industry to develop products that comply with these upcoming regulations. Additionally, this study evaluates the performance of plant-oil-based coatings not only in terms of preventing caking but also regarding dust formation, moisture absorption, crushing strength, and abrasion resistance. Two types of compound fertilisers, known for their caking tendencies, were tested with these plant-based coatings. Given the limited literature on this topic, this study offers valuable data on the caking tendencies of major compound fertilisers and contributes significantly through the development of plant-based coating agents, directly comparing them with commercial anti-caking agents, and applying specific experimental methods.

2 Experimental

2.1 Identification of control group fertilisers

Among NP (nitrogen-phosphorous) and NPK (nitrogen-phosphorous-potassium) fertilisers, formulations 20.20.0 (7/13) and 15.15.15 (15/0), were selected as control group fertilisers in compound type that are prone to caking, as shown in Table 1.

Fertiliser grades are represented as NPK values, indicating the contents of the three primary nutrients: nitrogen (N), phosphorus (P), and potassium (K) respectively. These values are typically displayed as a series of three numbers on the fertiliser packaging. For example, a fertiliser labelled 20.20.20 (7/13) would contain 20 % total nitrogen (with 7 % coming from ammonium, 13 % from urea), 20 % phosphorus (as P_2O_5), and 0 % potassium (as K_2O).[15] The total nitrogen amount in fertilisers refers to the sum of both ammonium nitrogen and urea nitrogen. These forms of nitrogen are sourced from various feedstocks, such as ammonium sulphate and urea, which are essential for plant growth as they provide crucial nutrients in different forms that plants can absorb and utilise. Ammonium nitrogen is readily available for plant uptake, while urea nitrogen must be converted into ammonium by microorganisms before it becomes available to plants.

Basic properties of the control group fertilisers were analysed as a preliminary step to characterise the fertilisers, following the methods outlined in Table 2.

Table 2 – Parameters of the control group fertilizers

Parameter	Test device	Test method
Particle size distribution	Retsch Sieve tester	TS 2832:2005[35]
Moisture content	Oven or Incubator	TS 2832:2005[35]
Bulk density	Volumetric container	TS 2832:2005[35]
Crystal structure	PANalytical Empyrean XRD	Operating voltage: 20–50 kV Operating current: 5–60 mA

2.2 Preparation of the anti-caking agents

Anti-caking agents were prepared using commercial patents[36] and various substances including two types of alkyl amines (stearylamine and oleylamine), plant-based oils (palm oil) and mineral oils (mineral oil), waxes (palm, paraffin), and fatty acids (lauric acid, coconut fatty acid), as detailed in Table 3.

2.3 Fertiliser coating process

The coating process was carried out by melting the anti-caking materials within the temperature range of 70–80 °C, and applying them in two different concentrations, 1000 and 1500 ppm. The process was carried out using 1 kg of uncoated fertiliser, to which 1000 mg (1000 ppm) and 1500 mg (1500 ppm) of coating materials were applied. The melted materials were sprayed onto the preheated fertiliser surfaces at 60 °C in an oven, using a syringe. After spraying, the fertilisers were rotated manually in plastic jars to ensure a more uniform and homogeneous coating.

2.4 Characterisation of coated fertiliser samples

2.4.1 Caking test

The accelerated caking test consisted of an initial climatic chamber test followed by a small bag caking test. Two consecutive climatic cycles were applied: i) 32 h at 20 °C and 80 % relative humidity, and ii) 72 h at 40 °C and 20 % relative humidity[37–38] in a JSR JSPC-200C model climatic chamber. After climatic conditioning, the samples were placed into the small bag storage test, where they were kept for four days under 0.28 kg cm^{-2} pressure in the test device, according to the IFDC S-106 method. Following the test, the samples were removed from their packages, and the caked portions were weighed.[39–40]

2.4.2 Moisture absorption and penetration test

To assess the moisture absorption (MA) and moisture penetration (MP) of the fertiliser samples, they were placed in open-mouthed cylindrical plastic tubes within a climatic chamber, ensuring exposure to ambient air. The samples were weighted after being exposed to environmental conditions of 30 °C and 80 % humidity for 72 h, in accordance with the IFDC S-100 standard.[15,37,39] MA was calculated using Eq. (1)[37,39], and is expressed as mg of moisture absorbed *per* unit surface area of the fertiliser.

$$\mathrm{MA} = \frac{\mathrm{FW} - \mathrm{OW}}{\mathrm{ES}} \cdot 1000 \tag{1}$$

MA, expressed in mg cm^{-2}, was calculated using the final weight (FW) of the sample in grams, the original weight (OW) of the sample in grams, and the exposed surface area (ES) of the sample in cm^2.

MP in the bulk fertiliser material was assessed by observing how far moisture travelled through the material after exposure to a controlled moisture environment in the cli-

Table 3 – Composition of the prepared anti-caking agents

Components/%wt	CAS No.	AC-1	AC-2	AC-3	AC-4	AC-5	AC-6	AC-7	AC-8
Stearylamine	124-30-1	10.00	10.00	–	–	10.00	10.00	–	–
Oleylamine	112-90-3	–	–	10.00	10.00	–	–	10.00	10.00
Coconut oil fatty acid	61788-47-4	10.00	15.00	10.00	15.00	10.00	15.00	10.00	15.00
Lauric acid	143-07-7	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
Diethanolamine	111-42-2	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Paraffin wax	8002-74-2	–	10.00	–	10.00	–	–	–	–
Palm wax powder	232-316-1	–	–	–	–	–	10.00	–	10.00
Mineral oil	8042-47-5	73.00	58.00	73.00	58.00	–	–	–	–
Palm oil	8002-75-3	–	–	–	–	73.00	58.00	73.00	58.00
SUM		100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

matic chamber. The measurement method involved filling a fixed-volume container with the fertiliser and identifying the wet region, which appeared darker. MP was measured along a vertical line in cm using a ruler.

Moisture holding capacity (MHC) was calculated from the MA data, expressed in $\mathrm{mg\,cm^{-2}}$, and the MP data, expressed in cm, according to Eq. (2)[37,39].

$$\mathrm{MHC} = \frac{\mathrm{MA}}{\mathrm{MP}} \tag{2}$$

2.5.3 Friability test

The abrasion resistance of the fertiliser samples was measured using a Pharmag PTF100 model friability tester, designed to simulate handling conditions. In this test, fertiliser granules were rotated in a drum at 50 revolutions *per* minute (rpm) for 120 s. The test procedure was adapted from the IFDC S-116 method based on the type and quantity of fertiliser.[15,37,39]

2.5.4 Crushing strength test

The crushing strength was measured using a Lutron FG-5000A and expressed as g *per* granule, according to the IFDC S-115 procedure.[15,37,39]

3 Results and discussion

3.1 Results for control group fertilisers

The particle size and distribution values of the fertilisers were determined using the sieve analysis method, and the results presented in Table 4. These results comply with the TS 2832 standard[35], which requires 90 % of the compound fertilisers to have a particle size between 1 and 4 mm, with a maximum of 3 % below 1 mm.

Table 4 – Particle size distribution of control group fertilisers

Particle size / %	20.20.0 (7/13)	15.15.15 (15/0)
4 mm and larger	0.50	0.20
1–4 mm	97.60	98.80
1 mm and smaller	1.90	1.00

One of the critical parameters influencing the caking mechanism is the moisture content within the granule structure, which manufacturers typically strive to minimise.[14] The moisture content of the fertiliser samples was found to be 0.8 % for 20.20.0 and 0.4 % for 15.15.15. These values comply with the TS 2832 standard for compound fertilisers, which sets a maximum moisture content of 1.0 % for granular fertilisers. These results also align with international and EU standards through ISO 8157:2022 (EN).[35,41] The bulk density results obtained were 1070 $\mathrm{kg\,m^{-3}}$ for 20.20.0 fertiliser, and 1032 $\mathrm{kg\,m^{-3}}$ for 15.15.15 fertiliser. According to the literature, granular NP-NPK fertilisers generally exhibit a bulk density range of 1000–1200 $\mathrm{kg\,m^{-3}}$.[15] An XRD analysis was performed to identify the crystal structure of the fertilisers. The crystallographic data for the 20.20.0 fertiliser, which primarily consists of monoammonium phosphate (MAP), is shown in Fig. 1.

The MAP structure in the 20.20.0 fertiliser is formed during the neutralisation reaction between ammonia and phosphoric acid, which are the primary feedstocks for NP compound fertilisers.[38] The crystallographic analysis for the 15.15.15 fertiliser, which primarily consists of diammonium phosphate (DAP), is shown in Fig. 2.

3.2 Characteristics of coated fertilisers

In this study, the characterisation of fertilisers coated with eight different anti-caking agents was performed at two coating concentrations: 1000 and 1500 ppm. The effect of the anti-caking agents was interpreted based on the evaluation of the results. To ensure coating homogeneity, fer-

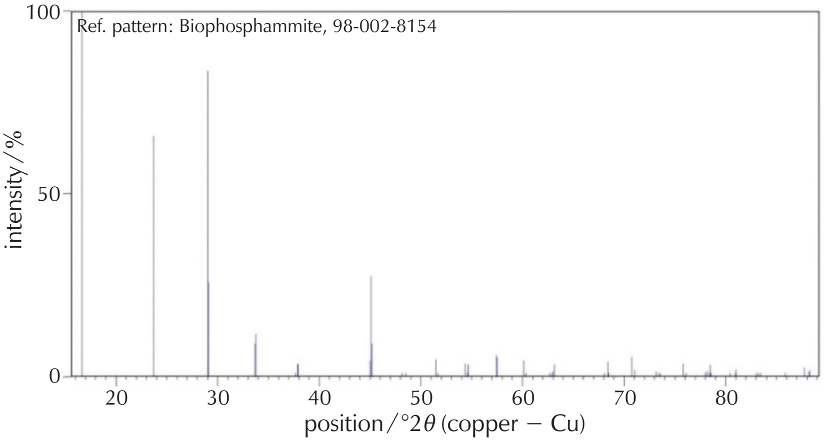

Fig. 1 – XRD crystallography of MAP structure in the NP-20.20.0 fertiliser

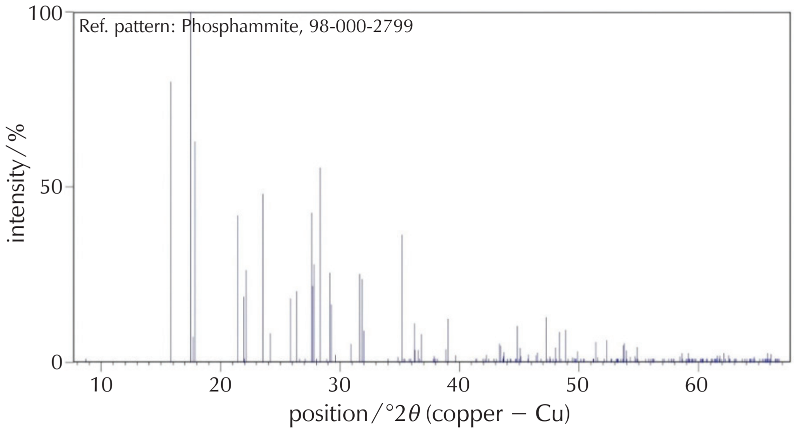

Fig. 2 – XRD crystallography of DAP structure in the NPK-15.15.15 fertiliser

tiliser samples were selected within a specific particle size range of 1–4 mm, aiding in more consistent application of the coating material. Preheating both the coating materials and fertiliser samples was implemented to improve adhesion of the coating agent and promote uniform distribution across the granule surfaces. Despite these efforts, we acknowledge that some variations in coating uniformity may still occur, and further studies using advanced techniques are recommended to more accurately assess and enhance the coating process.

3.2.1 Caking tendency

Caking is defined as the adhesion of fertiliser particles to one another due to phase changes or direct contact, resulting in the loss of free-flowing structure of the fertiliser granules.[18] Free-flowing fertiliser granules can consolidate into hard masses, causing a loss of function and overall quality.[8] This phenomenon presents significant challenges in industrial processes, including process interruptions, customer complaints, and inefficiencies in agricultural practices.[9] Anti-caking coatings that enhance the physical quality and maintain the free-flowing properties of fertilisers offer substantial benefits.[14] To assess the effectiveness of the prepared anti-caking agents, the fertiliser samples were exposed to high temperature and humidity conditions in a climatic test chamber using two consecutive climate cycles. Subsequently, the samples were tested in a small bag caking test under a certain pressure. The results on the caking tendencies of the tested fertilisers are presented in Table 5, comparing the uncoated fertiliser samples with two commercially available coatings, AC-R1 and AC-R2.

Table 5 – Caking tendencies of fertiliser samples

Anti-caking agent	Caking / %wt in 20.20.0 (7/13)	Caking / %wt in 15.15.15 (15/0)
Control (uncoated)	30.89	38.14
AC-R1 (reference)	3.97	13.40
AC-R2 (reference)	27.76	34.37
AC1-1000	0.00	11.06
AC1-1500	0.00	2.27
AC2-1000	0.00	4.99
AC2-1500	0.00	3.66
AC3-1000	0.00	2.99
AC3-1500	0.00	3.94
AC4-1000	1.39	14.70
AC4-1500	0.00	14.55
AC5-1000	1.36	17.45
AC5-1500	5.39	15.15
AC6-1000	1.69	11.79
AC6-1500	0.00	14.70
AC7-1000	14.97	13.42
AC7-1500	31.07	12.84
AC8-1000	4.09	12.04
AC8-1500	0.00	16.33

According to the results, the 20.20.0 (7/13) fertiliser exhibited a higher caking tendency than the 15.15.15 (15/0) fertiliser under all conditions. This phenomenon is related to the urea content in the 20.20.0 fertiliser and its critical relative humidity (CRH). The crystal salt structure and chemical composition of fertilisers contribute to their hygroscopic structure and specific CRH value, which indicates their moisture absorption capacity. CRH is defined as the minimum atmospheric relative humidity at which moisture absorption begins on the surface of the fertiliser. It is a key parameter influencing the caking tendency of fertilisers.[15] When a fertiliser is exposed to an environment where the relative humidity (RH) approaches its CRH, moisture absorption can commence on the fertiliser's surface. This moisture absorption leads to capillary condensation within the structure, forming liquid bridges between granules, which is a primary cause of caking. Once the RH equals or exceeds the CRH, the fertiliser can undergo a phase change, potentially leading to liquefaction of the granules, which makes them weak and prone to sticking together. In environments with RH above the CRH, the granule structure may transition to a liquid

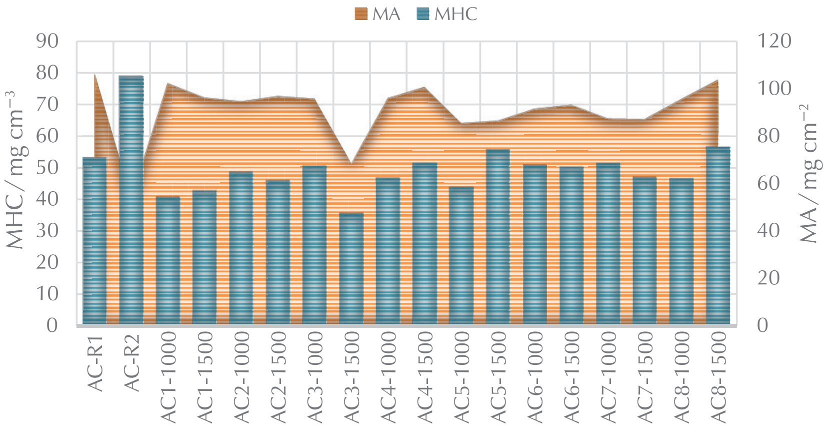

Fig. 3 – MA and MHC results for the 20.20.0 (7/13) fertiliser

phase, while at RH below the CRH, the fertiliser remains in a solid state. These interactions and phase changes between granules significantly affect the caking mechanism. Given that the 20.20.0 and 15.15.15 fertilisers exhibited different hygroscopic behaviours due to their distinct CRH values, they showed varying caking tendencies.[12] Additionally, the composition of the fertiliser is crucial for understanding caking tendencies. The CRH value of urea is between 70–75 % at 30 °C. However, this value decreases to 50–60 % when urea is combined with salts such as diammonium phosphate, potassium chloride, phosphate rock, and further decreases to 45–55 % when combined with ammonium sulphate.[15]

Regarding the effect of the anti-caking agents on caking, both uncoated fertilisers exhibited a higher caking tendency compared to the coated fertilisers. The caked amounts were 30.89 % for the 15.15.15 (15/0) fertiliser and 38.14 % for the 20.20.0 (7/13) fertiliser. The best performances for the 20.20.0 fertiliser were achieved with anti-caking agent containing stearylamine (AC1 and AC2) at both coating concentrations, and AC6 at a 1500 ppm coating concentration. Similarly, among the coatings containing oleylamine, AC3 at both coating concentrations and AC6 at a 1500 ppm were identified as the most effective applications. Stearylamine had a more significant impact on reducing the caking tendency of the 15.15.15 (15/0) fertiliser compared to oleylamine. For the 15.15.15 fertiliser, coatings with both petroleum-derived and plant-oil-derived anti-caking agents containing stearylamine resulted in caking in the range of 0–1.39 %. Given the commercial industry standard of a maximum 10% caking tendency, it is evident that AC7 (oleylamine, plant-oil) is not suitable for the 15.15.15 (15/0) fertiliser. However, AC8 (oleylamine, plant-oil and wax), which includes various wax derivatives, demonstrated improved performance. For the 20.20.0 (7/13) fertiliser, formulations combining mineral oil and stearylamine were effective in keeping caking below 5 %.

3.2.2 Moisture absorption and penetration

Moisture absorption and moisture holding capacities of the 20.20.0 fertiliser samples are presented in Fig. 3. The moisture absorption ranged from 53.65 to 115.41 mg cm^{-2}, demonstrating a moisture absorption capacity of 40–60 mg cm^{-3}. It has been reported that this value can reach 580 mg cm^{-2} when no coating is applied, with the moisture holding capacity achieving 15 mg cm^{-3}.[15] The results demonstrate that all coatings effectively protected the fertilisers from moisture, with the best performance observed with the coating containing oleylamine in mineral oil (AC3-1500) for the 20.20.0 fertiliser. Among the plant-based coatings, the most effective application was stearylamine (AC5-1000). In general, the average moisture absorption across all fertiliser surfaces coated with the prepared coatings was 92.30 mg cm^{-2}. However, the moisture-repellent performance of the prepared coatings was successful, in contrast to the AC-R2 coating.

The moisture absorption and moisture holding capacities of the 15.15.15 fertiliser samples are presented in Fig. 4. It was concluded that the 15.15.15 (15/0) fertiliser exhibited a lower potential for moisture absorption and penetration compared to the 20.20.0 (7/13) fertiliser. This difference is attributed to the chemical composition and the absence of urea in the fertiliser structure. Most of the applied coating materials demonstrated moisture absorption below 20 mg cm^{-2} and maintained moisture levels below 10 mg cm^{-3} throughout the entire volume. For urea-free ammonium sulphate-based NPK fertilisers, moisture absorption ranges from 270 to 365 mg cm^{-2}, and moisture holding capacity ranges from 7 to 9 mg cm^{-3}.[15] The AC7 coating at a concentration of 1000 ppm exhibited the highest moisture absorption with the lowest moisture holding capacity, indicating its effectiveness in preventing moisture penetration into the bulk of the fertiliser and demonstrating the best moisture-repellent performance for the 15.15.15 fertiliser. The moisture penetration depth (cm) for the 20.20.0 (7/13) fertiliser ranged from 2 to 2.5 cm, whereas for the 15.15.15 (15/0) fertiliser, it ranged from 1.5 to 6.3 cm.

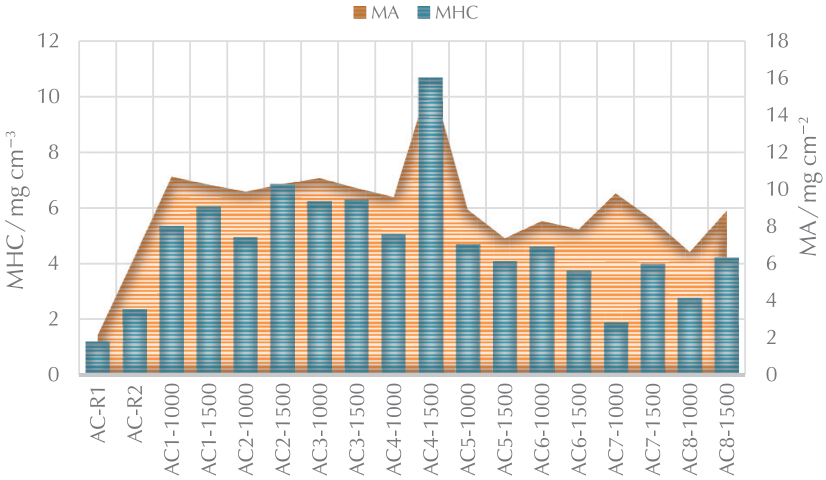

Fig. 4 – MA and MHC result for the 15.15.15 (15/0) fertiliser

3.2.3 Dust formation

The dust formation data following the handling test of fertilisers are presented in Fig. 5, expressed as weight percent (%wt). It was determined that the urea-containing fertiliser 20.20.0 (7/13) had a dust formation rate of 2.84 %, while the 15.15.15 fertiliser, which was urea-free, exhibited a dust formation rate of 1.91 %. Abrasion resistance can vary depending on the composition of salt contents. For example, the DAP 18.46.0 fertiliser, which contains ammonium sulphate and phosphate rock, has a dust formation potential that varies between 0.5 and 2.0 %.[15] Fig. 5 indicates that the amount of dust decreased with higher coating rates. This reduction is related to the film layer formed on the granule surface, which decreased friction and wear. Generally, the dusting of the 20.20.0 (7/13) samples was lower than that of the 15.15.15 fertilisers. Although there is higher dust formation, stronger adhesion can be achieved on the surface with the help of anti-caking agents. The results show that the film layer formed on the surface of the 20.20.0 (7/13) fertiliser by anti-caking materials is more resistant to abrasion. In summary, the best performance for both fertilisers was achieved with a 1500 ppm coating of the AC3 anti-caking agent.

3.2.4 Crushing strength

Crushing strength values are presented in Fig. 6, measured in g *per* granule. The two uncoated fertilisers exhibited crushing strengths in the range of 474 to 593 g *per* granule. It was observed that all anti-caking agents generally increased the crushing strength of the fertilisers, with the highest value recorded for a 1500 ppm concentration of AC4 (stearylamine, vegetable oil and wax) for both fertiliser types. The crushing strength of a fertiliser can vary based on its chemical composition, shape, surface, and moisture content.[42] These results are consistent with literature reports, indicating that ammonium sulphate-based granular fertilisers have crushing strengths ranging from 1500 to 2500 g *per* granule, while some fertilisers such as

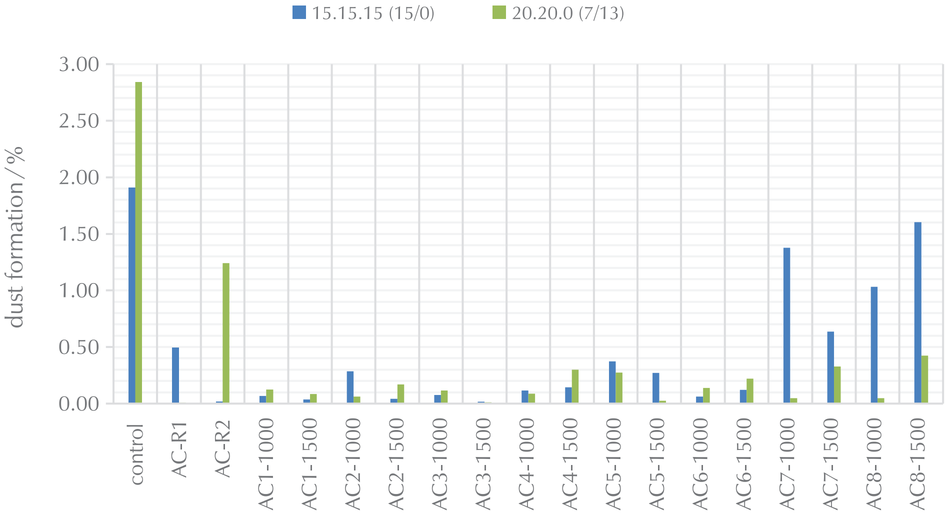

Fig. 5 – Dust formation of the coated 15.15.15 and 20.20.0 fertilisers

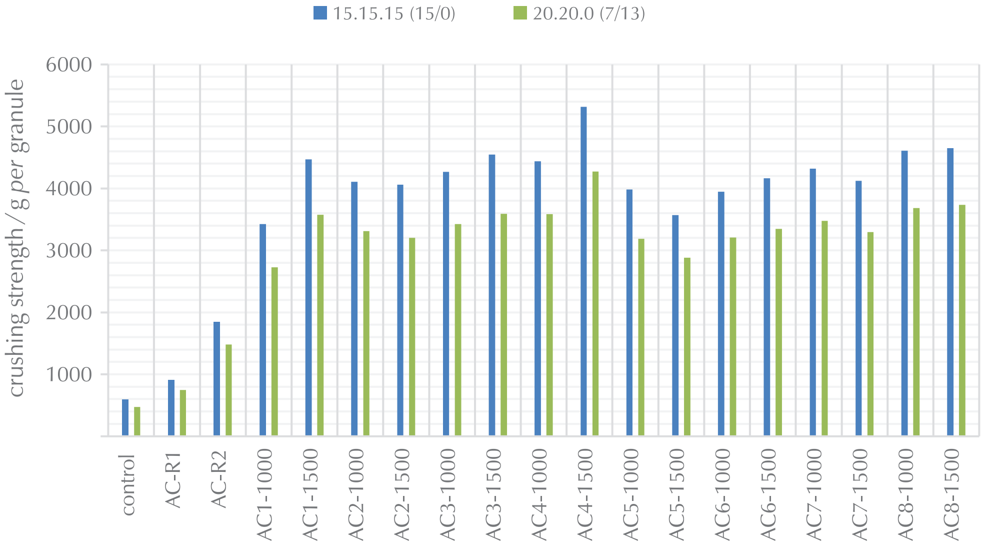

Fig. 6 – Crushing strength of the studied fertiliser samples

DAP have strengths of 3000 to 5000 g.[15] Conversely, the crushing strength of urea fertilisers is reported to be 1000 g for prills and 2500 g for granules.[37] Although anti-caking coatings do not directly affect the fertiliser formulations, they improve adhesion to the fertiliser surface and the film layer, which increases the resistance of the fertiliser granules to crushing pressure.[21] Generally, the 20.20.0 (7/13) fertiliser samples exhibited lower crushing strength compared to the 15.15.15 (15/0) fertiliser, which can be attributed to the urea content in the 20.20.0 fertilisers. Urea can weaken the granule structure, making it more prone to crushing into smaller particles and potentially causing dusting problems. This increased surface contact between granules can lead to more interactions, and, under harsh climatic conditions during transportation, result in easier caking. The primary issues of caking and dusting stem from the low crushing strength of the granules, which is significantly influenced by the urea content. To improve crushing strength, it is essential to ensure strong bonding within the fertiliser structure. Therefore, in addition to anti-caking coatings, the internal anti-caking agents, and granulation aids, such as binders, talc, or clay minerals, are often used.[15]

In general, these findings offer valuable insights into making the chemical processing of fertilisers more sustainable by exploring alternative, greener approaches to anti-caking agents. Although specific studies on the direct impact of green anti-caking agents are limited, broader research on sustainable alternatives suggests significant benefits. For instance, a systematic review of bio-based products indicates a 45 % reduction in greenhouse gas emissions compared to fossil-based counterparts.[43,44] The fertiliser industry, which consumes 2–3 % of global energy, exemplifies the substantial environmental impact of chemical production.[45] Transitioning to bio-based chemicals, including plant-based anti-caking agents, could therefore offer meaningful reductions in carbon emissions, aligning with the broader goals of industrial decarbonisation.

4 Conclusion

Caking in nitrogenous fertilisers raises a critical issue, impairing product quality and bringing financial losses. This study identifies a competitive edge by proposing plant-oil-based anti-caking agents as a sustainable alternative to petroleum-based options. For manufacturers, this solution offers regulatory compliance with upcoming EU restrictions and a step toward decarbonisation. While the initial costs of these green alternatives may be higher than conventional agents, their prolonged advantages, such as lowered environmental risk and regulation alignment, could make them a cost-effective option in manufacturing processes.

This study provides valuable insights into the formulation of plant-based anti-caking agents by exploring various components, such as surfactants, fatty acids, plant-based solvents, and wax derivatives. The experimental results reveal several important findings. Firstly, the interaction between stearylamine and plant oil resulted in a sufficiently hydrophobic film forming on the fertiliser surface, making the formulation of the AC3 (a combination of stearylamine and plant oil) the optimal anti-caking material. Most of the coating agents applied during the study exhibited moisture absorption levels below 20 $mg\,cm^{-2}$, with the moisture content maintained under 10 $mg\,cm^{-3}$ throughout the volume. The best performance, in terms of minimising moisture absorption and caking, was found with the 1500 ppm concentration of the AC3 anti-caking agent in both fertilisers studied. Additionally, oleylamine, when combined with plant-oil waxes, was effective in enhancing the protective barrier on the granule structure, contributing to improved performance.

This study addresses a critical issue for the fertiliser industry by focusing on the potential for a green transition in anti-caking agents to reduce CO_2 emissions while also tackling the solid quality problem of caking. The use of sustainable, bio-based materials aligns with global decarbonisation targets and offers practical solutions for industries looking to reduce their environmental impact while maintaining efficient production processes. Transitioning to greener alternatives, such as plant-based anti-caking agents, has the potential to significantly lower operational carbon footprints. This study not only highlights the environmental benefits but also emphasises the strategic advantage for industries that adopt sustainable practices, making it highly relevant for industry stakeholders.

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List of abbreviations

AC – anti-caking
CRH – critical relative humidity
DAP – diammonium phosphate
EU – European Union
IFDC – International Fertilizer Development Center
ISO – International Organization for Standardization
MAP – monoammonium phosphate
MA – moisture absorption
MP – moisture penetration
MHC – moisture holding capacity
NP – nitrogen-phosphorous fertiliser
NPK – nitrogen-phosphorous-potassium fertiliser
PAHs – polycyclic aromatic hydrocarbons
RH – relative humidity
RPM – revolution *per* minute
XRD – X-ray diffraction

References
Literatura

1. *S. Divya, I. Rusyn, O. Solorza-Feria, K. Sathish-Kumar,* Sustainable SMART fertilizers in agriculture systems: A review on fundamentals to in-field applications, Sci. Total Environ. **904** (2023) 166729, doi: https://doi.org/10.1016/j.scitotenv.2023.166729.
2. *J. Penuelas, F. Coello, J. Sardans,* A better use of fertilizers is needed for global food security and environmental sustainability, Agric. Food Secur. **12**(5) (2023) 5, doi: https://doi.org/10.1186/s40066-023-00409-5.
3. *M. A. Mathur, M. F. Dias, M. P. Mathur,* Importance of green technology in fertilizer quality improvement, Procedia Eng. **138** (2016) 308–313, doi: https://doi.org/10.1016/j.proeng.2016.02.089.
4. *E. Vermoesen, E. Cordeels, D. Schaubroeck, G. Brosens, S. Bodé, P. Boeckx, S. Van Vlierberghe,* Photo-crosslinkable biodegradable polymer coating to control fertilizer release, Eur. Polym. J. **186** (2023) 111835, doi: https://doi.org/10.1016/j.eurpolymj.2023.111835.
5. *B. Ni, M. Liu, S. Lu, L. Xie, Y. Wang,* Environmentally friendly slow-release nitrogen fertilizer, J. Agric. Food Chem. **59** (2011) 10169–10175, doi: https://doi.org/10.1021/jf202131z.
6. *P. Boberski, K. Torchała, H. Studnik, J. Wójcik, M. Główka, N. Kuźnik,* Biobased Materials for the Development of Biodegradable Slow-Release Fertilizers, Coatings **12** (8) (2022) 1215, doi: https://doi.org/10.3390/coatings12081215.
7. URL: Measuring-the-Sustainability-of-Fertilizer-Coatings-World-Fertilizer-JulAug-2020.pdf (fertiliser-society.org) (27. 5. 2024.)
8. *J. Aguilera, J. del Valle, M. Karel,* Caking phenomena in amorphous food powders, Trends Food Sci. Technol. **6** (5) (1995) 149–155, doi: https://doi.org/10.1016/S0924-2244(00)89023-8.
9. *J. A. S. Cleaver, G. Karatzas, S. Louis, I. Hayati,* Moisture-induced caking of boric acid powder, Powder Technol. **146** (1-2) (2004) 93–101, doi: https://doi.org/10.1016/j.powtec.2004.07.005.
10. *M. Chen, D. Zhang, W. Dong, Z. Luo, C. Kang, H. Li, J. Gong,* Amorphous and humidity caking: A review, Chin. J. Chem. Eng. **27** (6) (2019) 1429–1438, doi: https://doi.org/10.1016/j.cjche.2019.02.004.
11. *A. B. Albadarin, T. D. Lewis, G. M. Walker*, Granulated polyhalite fertilizer caking propensity, Powder Technol. **308** (2017) 193–199, doi: https://doi.org/10.1016/j.powtec.2016.12.004.
12. *M. Chen, S. Wu, S. Xu, B. Yu, M. Shilbayeh, Y. Liu, J. Gong,* Caking of crystals: Characterization, mechanisms and prevention, Powder Technol. **337** (2018) 51–67, doi: https://doi.org/10.1016/j.powtec.2017.04.052.
13. *U. Bröckel, M. Wahl, R. Kirsch, H. J. Feise,* Formation and growth of crystal bridges in bulk solids, Chem. Eng. Technol. **29**(6) (2006) 691–695, doi: https://doi.org/10.1002/ceat.200600066.
14. *R. J. Baird, S. Kabiri, F. Degryse, R. C. da Silva, I. Andelkovic M. J. McLaughlin,* Hydrophobic coatings for granular fertilizers to improve physical handling and nutrient delivery, Powder Technol. **424** (2023) 118521, doi: https://doi.org/10.1016/j.powtec.2023.118521.
15. *T. P. Hignett*, Fertilizer Manual. Vol. 15, Springer Science and Business Media, 2013, pp. 10–628.
16. *E. H. Novotny, R. de Oliveira-Silva, B. B. Mattos, I. Rech, P. Galvosas and T. J. Bonagamba,* Study of zeolite anti-caking effects for fertilisers by 1H low-field NMR, J. Magn. Reson. **342** (2022) 107264, doi: https://doi.org/10.1016/j.jmr.2022.107264.
17. *N. Surachaitanawat, D. Yulianto, S. Wirasate, C. Sirisinha, S. Raibhu M. Jariyaboon,* Development of new water-based anticaking agents for NPK fertilizers using response surface methodology, J. Appl. Polym. Sci. **140** (34) (2023) 54317, doi: https://doi.org/10.1002/app.54317.
18. *D. W. Rutland,* Fertilizer caking: mechanisms, influential factors, and methods of prevention, Fertilizer Research **30** (1991) 99–114, doi: https://doi.org/10.1007/BF01048832.
19. *G. M. Walker, T. R. A. Magee, C. R. Holland, M. N. Ahmad, J. N. Fox, N. A. Moffatt, A. G. Kells,* Caking processes in granular NPK fertilizer, Ind. Eng. Chem. Res. **37** (2) (1998) 435–438, doi: https://doi.org/10.1021/ie970387n.
20. *E. A. Bijpost, J. G. Korver*, New Developments in Fertiliser Coatings, International Fertiliser Society, 2016, pp. 1–24.

21. *A. Tyc, D. Nieweś, E. Pankalla, M. Huculak-Mączka, K. Hoffmann, J. Hoffmann,* Anti-Caking Coatings for Improving the Useful Properties of Ammonium Nitrate Fertilizers with Composition Modeling Using Box–Behnken Design, Materials **14** (19) (2021) 5761, doi: https://doi.org/10.3390/ma14195761.
22. *M. Hussein, A. Donaldson,* Monitoring of anti-caking solution preparation and loading during loadout treatment of potash using FT-NIR, J. Chem. Eng. Process Technol. **8** (3) (2017) 1000342, doi: https://doi.org/10.4172/2157-7048.1000342.
23. *A. Tyc, S. Penkala, M. Biegun, D. Nieweś, M. Huculak-Mączka, K. Hoffmann,* The effectiveness of commercial anticaking agents for ammonium nitrate fertilizers, Ecol. Chem. Eng. **26**(1-2) (2019) 127–135, doi: https://doi.org/10.2428/ecea.2019.26(1-2)11.
24. *B. I. Elzaki, Z. Y. Jun,* Relationships between structures of surfactants and their anti-hygroscopicity performance of ammonium nitrate particles, Arab. J. Chem. **13** (11) (2020) 7626–7636, doi: https://doi.org/10.1016/j.arabjc.2020.08.033.
25. *D. Chen,* Hygroscopicity of pharmaceutical crystals, PhD Thesis, 2009, University of Minnesota, Minneapolis, MN, USA.
26. *H. Li*, Design of amphiphilic anti-caking systems for solid particles, PhD Thesis, 2010, Martin Luther University, Halle-Wittenberg, Germany.
27. *A. T. Lawal,* Polycyclic aromatic hydrocarbons. A review, Cogent Environ. Sci. **3** (1) (2017) 1339841, doi: https://doi.org/10.1080/23311843.2017.1339841.
28. *J. A. R. Martinez, M. M. Blanch* (Kao Corp. SA.), U.S. Pat. Appl. US10815160B2, 27 Oct 2020.
29. *J. González-León, F. Simon, C. Besson, P. Nicol,* Variables Affecting Caking on Granular Phosphorous Containing Fertilizers, SYMPHOS 2019 – 5th International Symposium on Innovation & Technology in the Phosphate Industry, 2019, Morocco.
30. *S. Zhang, T. Shen, Y. Yang, X. Ma, B. Gao, Y. C. Li, P. Wang,* Novel environment-friendly superhydrophobic bio-based polymer derived from liquefied corncob for controlled-released fertilizer, Prog. Org. Coat. **151** (2021) 106018, doi: https://doi.org/10.1016/j.porgcoat.2020.106018.
31. *A. Tyc, D. Nieweś, S. Penkala, R. Grzesik, K. Hoffmann, J. Hoffmann,* Influence of anti-caking agents on the highly effective organic coatings for preventing the caking of ammonium nitrate fertilizers, Coatings **10** (11) (2020) 1093, doi: https://doi.org/10.3390/coatings10111093.
32. *S. Sun, W. Wang, F. Liu, L. Zhang, X. Fan,* Coating layer preparation with mixed vegetable oil and nutrient release regulation of fertilizer, Eur. Polym. J. **120** (2019) 109194, doi: https://doi.org/10.1016/j.eurpolymj.2019.08.021.
33. *S. Yuan, L. Cheng, Z. Tan,* Characteristics and preparation of oil-coated fertilizers: A review, JCR **345** (2022) 675–684, doi: https://doi.org/10.1016/j.jconrel.2022.03.040.
34. *M. J. McLaughlin, J. L. E. Degryse, R. J. Baird, R. C. Da Silva, J. Light* (Mosaic Co), U.S. Pat. Appl. US11807588, 07 Nov 2023.
35. TS 2832 :2005., Turkish Standard, Fertilizers-Compound fertilizer, Turkish Standards Institute, Ankara, Türkiye.
36. *J. A. R. Martinez, M. R. Fajardo* (Kao Corp. SA.), U.S. Pat. Appl. US8932490B2, 13 Jan 2015.
37. URL: https://ifdc.org/wp-content/uploads/2017/10/Publications-Catalog_10-18-17_JLFaccepted.pdf (29. 5. 2024.).
38. *Fertilizer Europe*, Production of NPK Fertilizers by the Mixed Acid Route, European Fertilizer Manufacturers' Association, 2000, Brussels, Belgium.
39. *J. W. Hofstee,* Physical properties of fertilizer in relation to handling and spreading, Wageningen University and Research. 1993, pp. 1–170.
40. URL: https://www.fertilizerseurope.com/wp-content/uploads/2007/08/Final-version-Storage-handling-and-transport-of-solid-fertilizers-18112015.pdf (29. 5. 2024.).
41. *ISO 8157:2022* International Organization for Standardization, Fertilizers, soil conditioners and beneficial substances, Technical Committee ISO/TC 134.
42. *M. Vashishtha, P. Dongara, D. Singh,* Improvement in properties of urea by phosphogypsum coating, Int. J. Chemtech Res. **2**(1) (2010) 36–44.
43. URL: https://joint-research-centre.ec.europa.eu/jrc-news-and-updates/emerging-bio-based-products-have-nearly-half-ghg-footprint-fossil-based-counterparts-2024-02-07_en (11. 9. 2024.).
44. *E. A. R. Zuiderveen, K. J. J. Kuipers, C. Caldeira, S. V. Hanssen, M. K. van der Hulst, M. M. J. de Jonge, A. Vlysidis, R. van Zelm, S. Sala, M. A. J. Huijbregts,* The potential of emerging bio-based products to reduce environmental impacts. Nat. Commun. **14** (1) (2023) 8521.
45. *G. Gaidajis, I. Kakanis,* Life cycle assessment of nitrate and compound fertilizers production – A case study, Sustde. **13** (1) (2020) 148.

SAŽETAK

Održive alternative tvarima za sprječavanje zgrudnjavanja gnojiva dobivenim iz nafte

*Aysu Kayalıoğlu** i *Ayla Özer*

U ovoj studiji ispitana je mogućnost zamjene konvencionalnih proizvoda protiv zgrudnjavanja, koji se dobivaju iz nafte, tvarima dobivenim iz biljne baze. Konvencionalni proizvodi protiv zgrudnjavanja dugotrajno zaostaju u tlu, a mogu se pretvoriti u štetne, mutagene oblike, predstavljajući tako rizik po okoliš. Da bi se rizik smanjio, razvijeni su ekološki prihvatljivi sastavi obloga koje su primijenjene na dvama različitim vrstama složenih gnojiva: 20.20.0 (7/13) i 15.15.15 (15/0), za koje je poznato da imaju izraženu sklonost zgrudnjavanja. Obložena gnojiva podvrgnuta su ispitivanjima da bi se procijenila njihova sklonost zgrudnjavanju, upijanje vlage, stvaranje prašine i otpornost na lomljenje. Gnojiva bez obloge pokazala su značajnu sklonost zgrudnjavanju od 30,89 do 38,14 % wt, s nastankom prašine između 1,91 i 2,84 % wt te otpornošću na lomljenje koja je iznosila između 473,8 i 593,0 g po granuli. Primjena obloga na biljnoj bazi dovela je do značajnog smanjenja sklonosti zgrudnjavanju u iznosu od 0 do 16,33 % wt, dajući rezultate usporedive s oblogama dobivenim iz nafte (od 0 do 17,45 % wt). Najznatnije poboljšanje bilo je pri primjeni obloge koja je sadržavala stearilamin, biljna ulja i voskove, što je rezultiralo granulama s otpornošću na lomljenje od 4274,2 do 5318,0 g po granuli i smanjenjem stvaranja prašine. Dodatno, obloge na biljnoj bazi pokazale su nisku apsorpciju vlage, ostajući ispod 20 $\mathrm{mg\,cm^{-2}}$.

Ključne riječi
Abrazija, sredstva protiv zgrudnjavanja, zgrudnjavanje, gnojiva, održive obloge

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